CLAIMS

1. An article comprising a substrate having at least one main surface coated with a multi-layer anti-reflection stack, wherein the multi-layer anti-reflection stack comprises, in the order indicated starting from the substrate:

a) a high index (HI) layer, having a refractive index n_D^{25} of 1.50 to 2.00 and resulting from the hardening of a first hardenable composition and comprising an organic-inorganic hybrid matrix resulting from the hydrolysis and condensation of at least one precursor compound bearing an epoxy or (meth)acryloxy group and at least two functions hydrolysable to silanol groups, within which at least one colloidal metal oxide or at least one colloidal chalcogenide or a mixture of these compounds is dispersed in the form of particles from 1 to 100 nm in diameter, preferably from 2 to 50 nm, and directly on this high index layer (HI):

b) a low index (LI) layer, having a refractive index n_D^{25} ranging from 1.38 to 1.44 obtained by deposition and hardening of a second hardenable composition and comprising the product of hydrolysis and condensation of:

(i) at least one precursor compound (I) comprising four hydrolysable functions per molecule of formula

$$Si(W)_4$$

in which the groups W, identical or different, are hydrolysable groups and provided that the groups W do not all represent at the same time a hydrogen atom,

(ii) at least one precursor silane (II) bearing at least one fluorinated group and comprising at least two hydrolysable groups per molecule,

said second composition comprising at least 10% by mass of fluorine in its theoretical dry extract (TDE), and the molar ratio I/ I + II of the precursor compound (I) to the sum of the precursor compound (I) + precursor silane (II) of the second composition being greater than 80%.

2. An article according to claim 1, wherein a main surface of the substrate is coated with an anti-abrasion layer or a layer of a primer

coating and a layer of an anti-abrasion coating, the anti-reflection stack being deposited onto the anti-abrasion coating.

3. An article according to any one of claims 1 or 2, wherein, in addition, silica (SiO_2) is dispersed in the matrix of the high index layer.

4. An article according to any one of the preceding claims, wherein the colloidal metal oxides and chalcogenides dispersed in the matrix of the high index layer are selected from the group comprising: TiO_2, ZnO, ZnS, ZnTe, CdS, CdSe, IrO_2, WO_3, Fe_2O_3, $FeTiO_3$, $BaTi_4O_9$, $SrTiO_3$, $ZrTiO_4$, MoO_3, CO_3O_4, SnO_2, bismuth-based ternary oxide, MoS_2, RuO_2, Sb_2O_4, $BaTi_4O_9$, MgO, $CaTiO_3$, V_2O_5, Mn_2O_3, CeO_2, Nb_2O_5, RuS_2.

5. An article according to any one of claims 1 to 3, characterised in that the particles of metal oxide dispersed in the matrix of the high index layer are constituted by a composite titanium oxide in the form of rutile.

6. An article according to any one of claims 4 or 5, wherein the mineral particles dispersed in the organic-inorganic hybrid matrix of the high index layer (HI) have a composite structure based on TiO_2, SnO_2, ZrO_2 and SiO_2.

7. An article according to any one of the preceding claims, wherein at least 60%, preferably at least 65% and, better still, at least 70% by mass of the theoretical dry extract (TDE) of the low index layer are derived from the precursor compound (I).

8. An article according to any one of the preceding claims, wherein the molar ratio I/I+II of the precursor compound (I) to the sum of the precursor compound (I) + precursor silane (II) is at least 85%, preferably 90% and, better still 95%.

9. An article according to any one of the preceding claims, wherein the hydrolysable groups W represent an OR, Cl or H group, R being alkyl.

10. An article according to any one of the preceding claims, wherein the hardenable composition of the low index layer (LI) comprises a tri- or dialkoxysilane different from the silanes of the precursor compound (I) of formula $Si(W)_4$ and from the precursor fluorosilane (II) in a proportion by weight not exceeding 10% of the total weight of the silanes present in said composition.

11. An article according to any one of claims 1 to 9, wherein the hardenable composition of the low index layer (LI) comprises only the silanes of the precursor (I) and the precursor fluorosilane (II).

12. An article according to any one of the preceding claims, wherein the anti-reflection stack comprises only a high index layer (HI) coated with a low index layer (LI).

13. An article according to any one of the claims 1 to 11, wherein the anti-reflection stack comprises at least three superimposed layers, starting from the substrate, a medium index layer (MI), a high index layer (HI) and a low index layer (LI), respectively, the medium index layer (MI) having a refractive index n_D^{25} of 1.45 to 1.80.

14. An article according to any one of the preceding Claim, wherein the layer of material of high refractive index (HI) has a refractive index greater than 1.7, preferably ranging from 1.72 to 1.82 and, better still, in the order of 1.77.

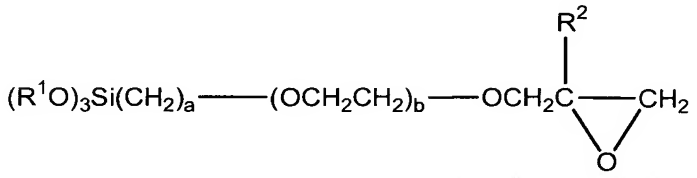
15. An article according to any one of the preceding claims, wherein the layer of material of high refractive index (HI) has a physical thickness ranging from 10 to 200 nm, and preferably ranging from 80 to 150 nm.

16. An article according to any one of the preceding claim, wherein the layer of material of low refractive index (LI) has a physical thickness ranging from 40 to 150 nm, and preferably in the order of 90 nm.

17. An article according to any one of the preceding claim, wherein the organic matrix of the composition (HI) is a hydrolysate of an epoxyalkoxysilane.

18. Optical article according to claim 17, wherein the epoxyalkoxysilane contains an epoxy group and three alkoxy groups, these latter being directly linked to the silicon atom.

19. Optical article according to claim 18, wherein the epoxyalkoxysilane corresponds to the formula (I):



(I)

in which:

R^1 is an alkyl group of 1 to 6 carbon atoms, preferentially a methyl or ethyl group,

R^2 is a methyl group or a hydrogen atom,

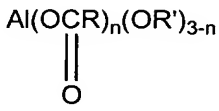
a is an integer between 1 and 6,

b represents 0.1 or 2.

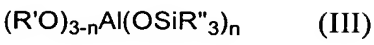
20. An article according to claim 19, wherein the epoxyalkoxysilane is γ-glycidoxypropyltrimethoxysilane.

21. An article according to any one of the preceding claims, wherein the hardenable composition of the high index layer (HI) is combined with a catalyst constituted of an aluminium compound selected from:

- aluminium chelates,
- compounds of formula (II) or (III):



(II)

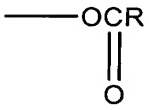


(III)

in which:

R and R' are linear or branched chain alkyl groups of 1 to 10 carbon atoms,

R'' is a linear or branched chain alkyl group of 1 to 10 carbon atoms, a phenyl group, a group



in which R has the meaning specified above, and n is an integer from 1 to 3,

an organic solvent, the boiling point T of which, at atmospheric pressure, is ranges from 70°C to 140°C, being present in the hardenable composition (HI) when the catalyst is an aluminium chelate.

22. An article according to claim 21, wherein the catalyst of the hardenable composition (HI) is an aluminium chelate, and preferably aluminium acetylacetonate.

23. An article according to any one of the preceding claims, wherein the precursor compound (I) of the second hardenable composition (LI) is a tetraalkoxysilane, and preferably a tetraethoxysilane.

24. An article according to any one of the preceding claims, wherein precursor silane (II) is selected from perfluorosilanes.

25. An article according to any one of the preceding claims, wherein the substrate is a substrate made of an organic glass, optionally provided with an anti-abrasion coating and/or a impact-resistant coating.

26. An article according to any one of the preceding Claim, wherein it further comprises a hydrophobic anti-fouling coating deposited onto the anti-reflection coating.

27. A process for the manufacture of an article according to any one of claims 1 to 26, comprising the steps of:

- depositing onto at least one of the surfaces of the substrate optionally coated with an anti-abrasion coating or a primer layer and an anti-abrasion coating at least one layer of material of high refractive index (HI), by application and then hardening of a first hardenable composition (HI) comprising an organic-inorganic hybrid matrix resulting from the hydrolysis and condensation of at least one precursor compound bearing an epoxy or (meth)acryloxy group and at least two functions hydrolysable to silanol groups, within which at least one metal oxide and/or at least one chalcogenide is dispersed in the form of particles having a diameter of 1 to 100 nm, and preferably of 2 to 50 nm,
- depositing onto said layer (HI) of at least one layer of material of low refractive index (LI), by application then hardening of a second hardenable composition (LI), preferably free of any mineral charge and comprising the product of hydrolysis and condensation of:

(i) at least one precursor compound (I) comprising 4 hydrolysable functions per molecule of formula

$$Si(W)_4$$

in which the W groups, identical or different, are hydrolysable groups and provided that the W groups do not all represent at the same time a hydrogen atom,

(ii) at least one precursor silane (II) bearing at least one fluorinated group and comprising at least two hydrolysable groups per molecule,

said second composition comprising at least 10% by mass of fluorine in its theoretical dry extract (TDE), and the molar ratio I/ I + II of the precursor compound (I) to the sum of the precursor compound (I) + precursor silane (II)) of the second composition being greater than 80%.

28. A process according to claim 27, wherein the layers of material of high refractive index (HI) and low refractive index (LI) are deposited by means of dip coating or by means of spin coating, and preferably by spin coating.

29. A process according to claim 27 or 28, wherein it includes, between the deposition of the layer of material of high refractive index (HI) and that of the layer of material of low refractive index (LI), a surface treatment of the layer (HI) in order to prepare the surface for the deposition of the layer (LI).

30. A process according to claim 29, wherein the treatment of the surface of the layer of material of high refractive index (HI) is an infrared treatment, followed by cooling by means of a stream of air at ambient temperature.

31. A process according to any one of claims 27 to 30, wherein the anti-reflection stack is a triple layer stack (MI/HI/LI) comprising successively, and in the order starting from the substrate, a layer of material of medium refractive index (MI), a layer of material of high refractive index (HI) and a layer of material of low refractive index (LI).

32. A process according to any one of the claims 27 to 31, wherein the layer of material of high refractive index (HI) has a refractive index of 1.72 to 1.82, and preferably in the order of 1.77.

33. A process according to any one of claims 27 to 32, wherein the layer of material of low refractive index (LI) has a refractive index varying from 1.38 to 1.44, and preferably in the order of 1.43.

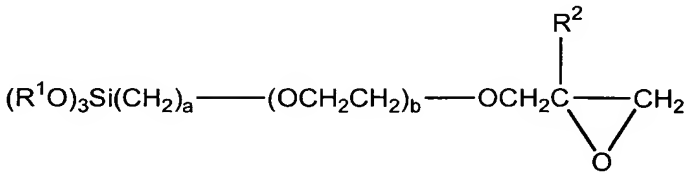
34. A process according to any one of claims 27 to 33, wherein the layer of material of high refractive index (HI) has a physical thickness ranging from 10 to 200 nm, and preferably from 80 to 150 nm.

35. A process according to any one of claims 27 to 34, wherein the layer of material of low refractive index (LI) has a physical thickness ranging from 40 to 150 nm, and is preferably in the order of 90 nm.

36. A process according to any one of the claims 27 to 35, wherein the precursor compound of the first hardenable composition (HI) is a hydrolysate of an epoxyalkoxysilane

37. A process according to claim 36, wherein the epoxyalkoxysilane contains an epoxy group and three alkoxy groups, these latter being directly linked to the silicon atom.

38. A process according to claim 37, wherein the silane with an epoxy group is an epoxysilane corresponding to the formula (I):



(I)

in which:

R^1 is an alkyl group of 1 to 6 carbon atoms, preferentially a methyl or ethyl group,

R^2 is a methyl group or a hydrogen atom,

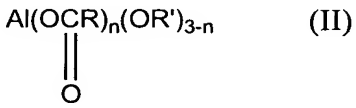
a is an integer between 1 and 6,

b represents 0.1 or 2.

39. A process according to claim 38, wherein the epoxysilane is γ-glycidoxypropyltrimethoxysilane.

40. A process according to any one of claims 27 to 39, wherein the hardenable composition (HI) is combined with a catalyst constituted by an aluminium compound selected from:

- aluminium chelates,
- compounds of formula (II) or (III):



(II)

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in which:

R and R' are linear or branched chain alkyl groups of 1 to 10 carbon atoms,

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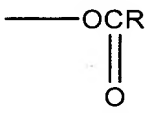

in which R has the meaning specified above, and n is an integer from 1 to 3,

an organic solvent, the boiling point T of which, at atmospheric pressure, ranges from 70°C to 140°C, being present in the hardenable composition (HI) when the catalyst is an aluminium chelate.

41. A process according to claim 40, wherein the catalyst of the composition (HI) is an aluminium chelate, and preferably aluminium acetylacetonate.

42. A process according any one of claims 27 to 41, wherein the precursor compound (I) of the composition of low index (LI) is a tetraalkoxysilane, and preferably a tetraethoxysilane.

43. A process according to any one of claims 27 to 42, wherein the precursor silane (II) of the composition of low index (LI) is a perfluorosilane.